Recycling of the Supporting Electrolyte Tetra(*n*-butyl)ammonium Hexafluorophosphate from Used Electrolyte Solutions

Stefan Dümmling,
Emerich Eichhorn,
Susanne Schneider,
Bernd Speiser, and*
Marc Würde
Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18,
D - 72076 Tübingen,
Germany

** Corresponding author.*
E-mail:
bs@echem3.orgchemie.chemie.uni-tuebingen.de

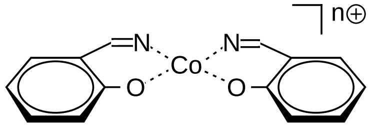
*Procedures are designed for the recycling of the supporting electrolyte tetra(*n*-butyl)ammonium hexafluorophosphate (TBAHFP) from electrolyte solutions used for electroanalytical or electrosynthetic purposes. The quality of the recycled product is assessed from cyclic voltammograms and is comparable to TBAHFP from the original synthesis.*

A supporting electrolyte (SE) is used to increase conductivity in the majority of all electroanalytical or electrosynthetic experiments in non-aqueous solutions (1,2). While some experiments have recently been performed with microelectrodes under conditions where no SE is deliberately added (3), it is common practice to have present a large excess of these salts ($c_{SE} \approx$ 0.1 M) relative to the substrates investigated (typical for electroanalytical work: $c_{substrate} \approx 10^{-4}$ M). Excess SE affects the current in the bulk of the solution, which is maintained mostly by the ions of the SE, and migration effects on charged substrates can be neglected (4). The SE can also have effects on the double layer.

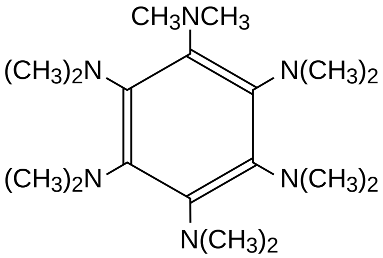
Although some SEs are available commercially, they are often routinely synthesized in electrochemical laboratories because the procedures are usually simple and the precursors are much cheaper than the commercial products.

In our laboratory, large quantities of used electrolytes from electroanalytical and electrosynthetic experiments had to be disposed of, so we tested the possibility of separating and recycling the SE from these solutions. If the quality of such a recycled SE was satisfactory for use in further experiments, and if the recycling procedure was not significantly more involved than the synthesis of a new SE, it would be possible to decrease not only the costs for the purchase of the salts or their precursors but also the amount of liquid wastes produced.

In this manuscript, we describe how the widely used SE tetra(*n*-butyl)ammonium hexafluorophosphate (TBAHFP) can be recycled from dimethylformamide (DMF), acetonitrile, dichloromethane, or pyridine solutions of organometallic and organic substrates. Electrolyte batches containing TBAHFP from two series of experiments were used: a) from investigations of ferrocene (fc), *N*,*N'*-bis(salicylidene)ethylene-diaminato-cobalt (II)/(III), Co(salen) **1**, and its one-electron oxidation product [Co(salen)]$^+$,**1**$^+$, in various solvents (5); b) from analyses of hexaaminobenzene derivatives [e.g. hexakis(dimethylamino)benzene, **2** (see structures below)] in CH_2Cl_2 and CH_3CN (6). We will show that the quality of the recycled product is similar to that of TBAHFP from the original synthesis by comparing background voltammograms and current potential curves of several redox active compounds.



1: Co = Co^{II}, *n* = 0; **1**$^+$: Co = Co^{III}, *n* =1



2

Experimental

General

Cyclic voltammetry was performed in a three-electrode cell equipped with a Pt working electrode tip (BAS, electroactive area $A \approx 0.08$ cm^2), a Pt wire counter electrode (fitted with a ground glass joint) and a Ag/Ag^+ reference (0.01 M $AgClO_4$ in acetonitrile/0.1 M TBAHFP) connected to the cell by a classical or double-reference (7) Haber-Luggin capillary. All potentials are referred to an external fc/fc^+ standard in the respective electrolyte. A BAS 100A electrochemical analyzer or a BAS 100B/W electrochemical workstation were used to generate the potential sweep and to record the current signal. In the latter case, data were collected on a personal computer. BAS 100A plots were digitized later. Plots were generated from all digital data with the X Window system-based program XEASI (8) on a UNIX workstation .

Purification of Solvents

N,N-*Dimethylformamide* was fractioned three times *in vacuo* (P_2O_5 was added before the first fractionation) and stored in the dark.

Pyridine was kept over KOH for several weeks and distilled just before use.

Acetonitrile was distilled from P_2O_5, NaH, and P_2O_5 again. The resulting solvent was passed through a column with Al_2O_3 (neutral, dried at 140°C, and stored under Ar).

Dichloromethane was distilled from P_2O_5 and then K_2CO_3 before it was passed through an Al_2O_3 column (activation as given above).

Preparation of Electrolyte Solutions

In most cases, the electrolyte was prepared from 1.94 g TBAHFP and placed in a Schlenk flask. Air was removed by evacuating and filling with Ar three times before 50 mL of the solvent (dried as described above) were added in an Ar counter current. The electrolyte was deoxygenated by three freeze-pump-thaw cycles.

Cell Assembly

The glass cell was usually dried at 140°C, equipped with the counter electrode, evacuated, and filled with Ar three times. A volume of 20 mL of electrolyte was added against an Ar flow. Then, the working and the reference electrode were introduced. After background curves were recorded, weighed samples of the substrates were added against an Ar flow.

Synthesis of Tetra(*n*-butyl)ammonium Hexafluorophosphate.

We synthesized TBHFP based on a procedure cited by Fry (2,9) and improved and optimized by Salbeck (10), Fry (11), as well as in our laboratory.

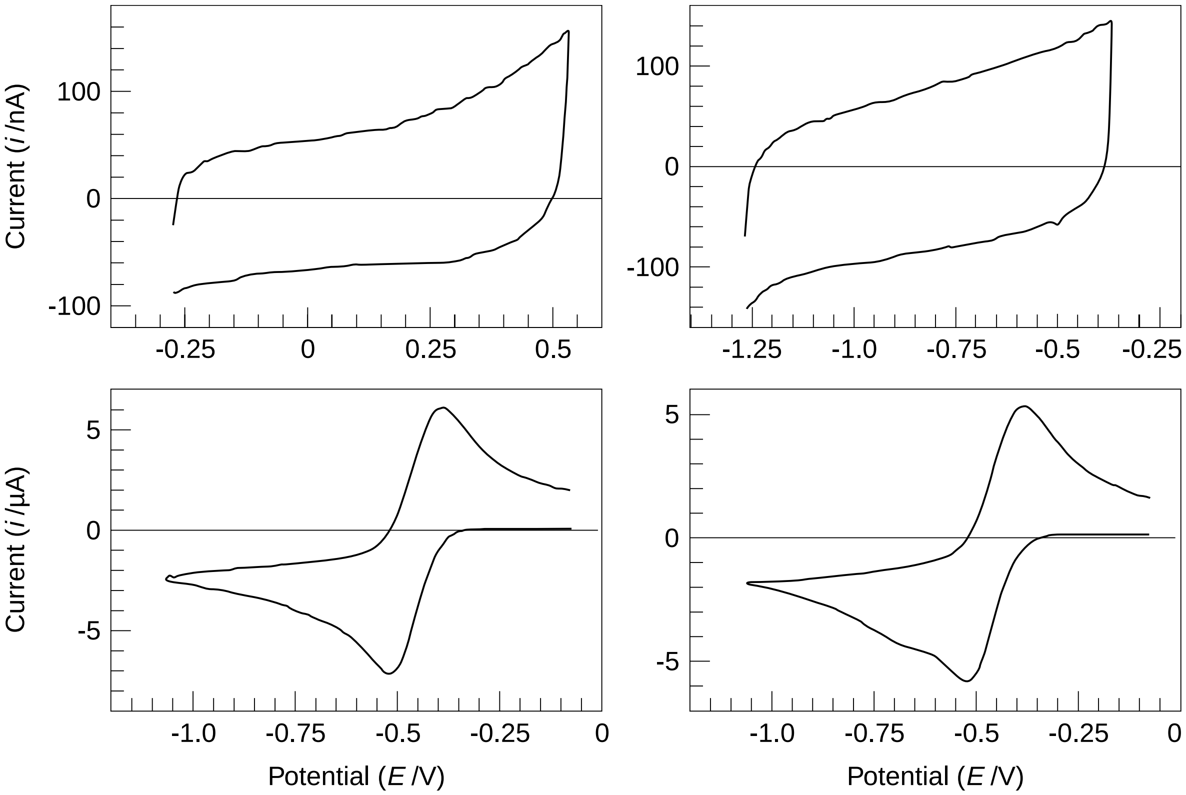
A 100 g sample (0.31 mol) of NBu_4Br (Fluka, purum) was dissolved in 250 mL acetone (for synthesis) and then mixed with 50 g (0.4 mol) NH_4PF_6 (Fluka, purum) in 350 mL acetone. Colorless NH_4Br precipitated and was filtered off (glass funnel with folded filter or Büchner funnel). The clear solution was concentrated to a volume of approximately 200 mL with a rotary evaporator. The desired TBAHFP was then precipitated by the addition of water until a volume of approximately 2 L was reached. After separation, the precipitate was redissolved in a solution of 5 g (0.04 mol) NH_4PF_6 in 200 mL of acetone (in some preparations more acetone had to be added in order to dissolve all of the solid). Again, water was added and the precipitate collected. The colorless product was recrystallized four times from a mixture of ethanol/water (3:1, v/v) and finally dried for 48 h at 100°C *in vacuo*. Yield: 90-102 g (75-85% of the theoretical amount).

Recycling of the Supporting Electrolyte

From Co(salen) solutions. A volume of 1.75 L electrolyte (mixture of solutions in acetonitrile, CH_2Cl_2, DMF, pyridine, and propylene carbonate; concentration of TBAHFP: 0.1 M; contaminated with fc, Co(salen), $[Co(salen)]^+$, its derivatives and possibly decomposition products such as the salen ligand, salicylic aldehyde, and ethylenediamine, in concentrations up to 1 mM) was concentrated by distillation to approximately 200 mL. After cooling to room temperature, the SE was precipitated by the addition of 400 mL water or ethanol (12) forming a dark brown amorphous mass, which was collected, air-dried and recrystallized from 200 mL ethanol. The mother liquor was rejected. The crystalline product was recrystallized from ethanol until the mother liquor became colorless (usually 2 or 3 further recrystallizations; allow to cool down slowly; collect mother liquor, see below). Finally, three additional recrystallizations from ethanol yielded after 48 h of drying at 100°C *in vacuo* 35-40 g colorless crystals (50-60% of the SE contained in the electrolyte solution).

From the collected solutions, 5-10 g more of raw TBAHFP could be separated by evaporation of the solvent to a volume of 200 mL. This raw SE was usually purified together with the product of the next batch of electrolyte recycling. The evaporated ethanol may be reused in further recrystallizations.

From hexakis(dimethylamino)benzene solutions. The solution [≈ 1 L; mixture of CH_2Cl_2 and acetonitrile; concentration of TBAHFP: 0.1 M; contaminated with fc and with hexakis(dimethylamino)benzene and derivatives, as well as their oxidation products] was evaporated to dryness with a



F1

Cyclic voltammograms in electrolytes prepared from TBAHFP recycled from Co(salen) experiment solutions; Pt electrode, A ≈ 0.08 cm^2, all potentials vs. fc/fc^+ in the respective solvent; top, left: DMF/0.1 M TBAHFP background voltammogram, ν = 0.05 V/s; top, right: pyridine/0.1 M TBAHFP background voltammogram, ν = 0.05 V/s; bottom, left: 0.25 mM $Co(salen)ClO_4$ in DMF/0.1 M TBAHFP, ν = 1.0 V/s; bottom, right: 0.25 mM $Co(salen)ClO_4$ in DMF/0.1 M TBAHFP, ν = 1.0 V/s, with basic impurity.

rotary evaporator. The solid residue was recrystallized from ethanol/water and the resulting crystals were washed with 150 mL water. Three further recrystallizations from ethanol/water yielded after drying for 48 h at 100°C and 3 x 10^{-2} mbar 32.3 g pure TBAHFP (85% of the amount in the starting solution).

Results and Discussion

TBAHFP can be recycled from used electrolyte solutions with good yields. The procedures described differ mainly in the removal of the electrolyte solvents and in the solvent applied for recrystallization. Distillation or evaporation of the solvent can be used successfully. Distillation may be advantageous if solvents with high boiling points are present (e.g., propylene carbonate in the first procedure).

TBAHFP is essentially insoluble in water. Therefore, the addition of water to the solvent during recrystallization increases the yield of the recycled SE. Any residual water can be easily removed during the final drying stage.

The recycling procedures used involve only a minor overhead compared to the original synthesis of TBAHFP. The main time-consuming manipulations, both in the synthesis and the recycling protocols, are the recrystallization steps. Fortunately, TBAHFP yields pure and good quality crystals upon slow cooling of the saturated ethanol or ethanol/water solutions.

The starting solutions were highly colored in both cases due to the contaminants [Co (salen), dication of hexakis(dimethylamino)benzene (13)]. Consequently, any remaining impurities could easily be detected by visual inspection.

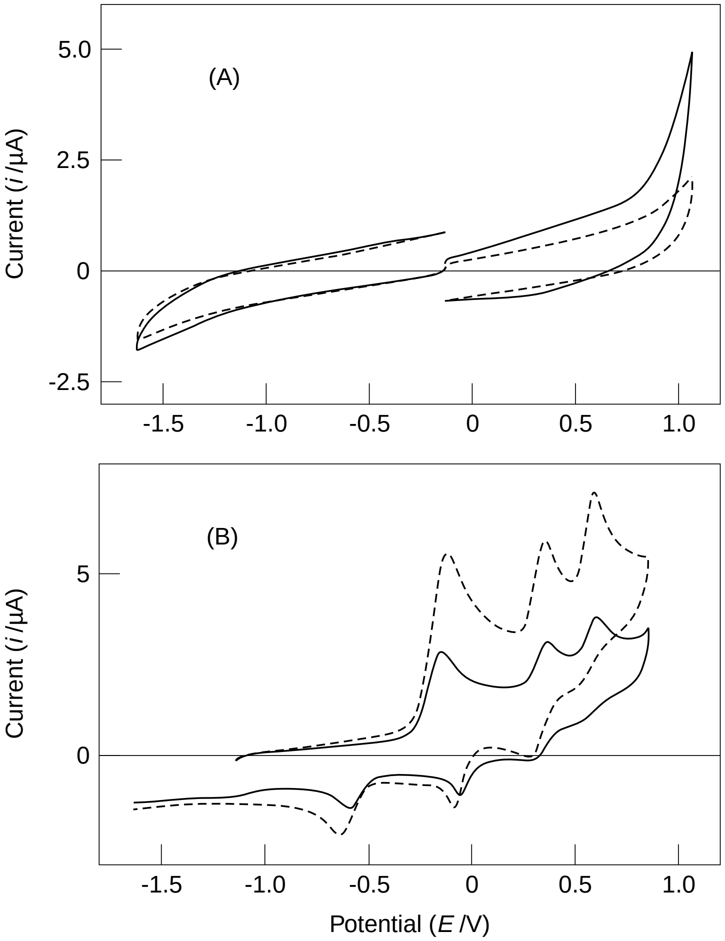
Of course, the quality of the recycled TBAHFP for use in electrochemical experiments can finally be assessed by recording the cyclic voltammetric curves and comparing them with those from electrolyte solutions prepared with the original SE. Thus, both background voltammograms and voltammograms of substrate solutions were recorded for the SE from the original synthesis and the recycling procedure (***F1*** and ***F2***).

The background curves in DMF and pyridine electrolytes prepared from recycled TBAHFP (***F1***, top) do not show any signals due to electroactive contaminants. Cyclic voltammograms of $[Co(salen)]^+$ consist of a simple, well-defined, quasi-reversible peak couple (***F1***, bottom left). These were identical to current/potential curves recorded in electrolytes prepared from original TBAHFP. The cation $[Co(salen)]^+$ is a Lewis acid (14), and it is extremely susceptible to reactions with bases. Presence of basic impurities, even in small concentrations, causes a splitting of the reduction peak (5). An example is shown in ***F1***, bottom right, where DMF of a non-satisfactory purity was used. The voltammograms clearly indicate the absence of any basic impurities in the electrolytes prepared from the recycled SE.

In ***F2A***, background cyclic voltammograms of electrolytes prepared with new and recycled TBAHFP in mixtures of CH_2Cl_2 and acetonitrile (1:1) are presented,

F2

Cyclic voltammograms in CH_2Cl_2/CH_3CN (1:1) electrolytes, Pt electrode, $A \approx 0.08\ cm^2$, all potentials vs. fc/fc^+; a) background voltammograms, electrolyte from new TBAHFP (0.1 M; solid line) and TBAHFP recycled from hexakis(dimethylamino)benzene experiment solutions (0.1 M; broken line); b) voltammograms of ***2****; solid line: c = 0.06 mM* ***2****, v = 0.1 V/s, new TBAHFP (0.1 M); broken line: c = 0.24 mM* ***2****, v = 0.1 V/s, recycled TBAHFP (0.1 M).*



extending over the entire accessible potential window. In this case, again, the curves of the recycled SE do not indicate any remaining impurities.

Cyclic voltammograms of hexakis(dimethylamino)benzene in this solvent system (***F2B***; oxidation occurs in three stages up to a tetrakation (6)) also do not reveal significant differences between electrolytes prepared from new or recycled SE. The slight potential shifts of the peaks on the reverse scan are within the reproducibility observed with this system.

The recycling procedure described here is successful since TBAHFP crystallizes very well from ethanol. Addition of water decreases the solubility of this SE and increases the yield.

If other contaminants were present in the electrolyte solutions, the recycling procedure may not be as effective as in the cases discussed, particularly, if the solubility behavior of the contaminants were similar to that of TBAHFP. In such cases, one trial recycling run can easily show the quality of the recycled SE from cyclic voltammograms.

Conclusion

Good quality TBAHFP can be recycled from used solutions of this SE after electroanalytical or electrosynthetic experiments. Only minor overhead is involved as compared to the original synthesis of TBAHFP. Thus, the recycling procedure can be recommended to decrease the purchase and disposal costs of TBAHFP as well as the volume of liquid wastes produced.

Acknowledgments

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